

SUMMARY REPORT

REPORT

CONTRACT NO. F04606-89-D-0034/DO Q807

Advanced Technology

Cleaning Methods

for High-Precision Cleaning

of Guidance System

Components

To

The Aerospace Guidance and

Metrology Center

Newark Air Force Base, OH

September 3, 1993

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Summary Report

Contract No. F04606-89-D-0034/DO Q807

on

**Advanced Technology Cleaning Methods
for High-Precision Cleaning of Guidance System Components**

to

**Department of the Air Force
Aerospace Guidance and Metrology Center
Newark AFB, OH 43057-0024**

September 3, 1993

by

Craig T. Walters, Jeff L. Dulaney, and Bernerd E. Campbell

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September 3, 1993

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Department of the Air Force
AGMC/EM
Newark Air Force Base, OH 43057-0024

Dear Al:

**CONTRACT NO. F04606-89-D-0034/DO Q807
ADVANCED TECHNOLOGY METHODS FOR HIGH-PRECISION CLEANING OF
GUIDANCE SYSTEM COMPONENTS**

Reference: Contracts Data Requirements List, Sequence No. A0002

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If you have any questions about the enclosed report, please contact me at 614-424-5689.

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Research Leader
Applied Physics Group

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EXECUTIVE SUMMARY

This report summarizes research activity undertaken for the Aerospace Guidance and Metrology Center (AGMC) at Newark Air Force Base, Ohio in support of their goal of finding methods, materials, and technologies that will permit them to perform their maintenance mission with greatly reduced utilization of solvents that are hazardous to workers and the environment. The maintenance of guidance system components often entails removal of organic adhesives and low residue cleaning of high value precision metal parts in the disassembly, repair, and preparation for reassembly stages. In the past, strong solvents that may be toxic, carcinogenic, or detrimental to the environment have been used effectively for this purpose.

The objective of the research conducted under this program was to assess the possible role of advanced technology cleaning methods (such as laser and plasma cleaning) in maintenance of high-precision guidance system components and to provide preliminary experimental data to support this assessment. The research included identification of candidate cleaning tasks, assessment of the advanced cleaning technology base, and experimental demonstration of laser cleaning approaches.

Plasma cleaning was found to be fairly well-developed as a technology, but of limited usefulness in most of AGMC's cleaning tasks because of the extremely slow material removal rates. It might be used for large area adhesive bond preparation if only a thin contaminant film is present.

Most of the research was devoted to demonstrating laser cleaning techniques that would be widely applicable and have high leverage in hazardous solvent use reduction at AGMC. A new laser cleaning technique was discovered that can be used to remove residual cured epoxy layers and patches up to several hundred micrometers thick bonded to metal substrates. The method is quick and efficient, uses no liquids, can be precisely applied to a specific area, and generates no effluent vapor. For long laser pulses (1.06 μm , 1 ms), the surface temperature of the metal rises to no more than about 200 C for a brief instant. A

Laser removal of particulate contaminants for final assembly cleaning was also investigated. In this method, a transient liquid film consisting of a water/alcohol mixture is deposited on the surface prior to laser exposure ($1.06\ \mu\text{m}$, 10 ns). Micron and submicron size particles are blown off of the surface by explosive vaporization of the liquid via heat conducted from the substrate. This technique was successfully demonstrated in the program for SS-304 and 52100 bearing steel substrates.

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1.0 Introduction

This report summarizes research activity undertaken for the Aerospace Guidance and Metrology Center (AGMC) at Newark Air Force Base, Ohio in support of their goal of finding methods, materials, and technologies that will permit them to perform their maintenance mission with greatly reduced utilization of solvents that are hazardous to workers and the environment. The maintenance of guidance system components often entails removal of organic adhesives and low residue cleaning of high-value precision metal parts in the disassembly, repair, and preparation for reassembly stages. In the past, strong solvents that may be toxic, carcinogenic, or detrimental to the environment have been used effectively for this purpose.

In light of major changes in cleaning procedures being brought about by the elimination of the use of chlorofluorocarbons (CFC's) and other hazardous chemicals by the Air Force, it is of critical importance to examine all technologies that will lead to effective and productive cleaning procedures under the new operational constraints. In many cases where parts to be cleaned have narrow crevices or highly inaccessible surfaces with




Some of the technologies that will likely remain the preferred

2.0 Identification of Candidate Cleaning Tasks

At the beginning of the program, Battelle staff reviewed a number of cleaning task candidates with AGMC staff to identify those that might be amenable to laser or plasma cleaning processes. For this initial phase, the candidate list was not intended to be exhaustive but, rather, representative of high volume repair activity that could greatly benefit from the alternative cleaning technology. A brief description of these tasks is given below.

2.1 Epoxy Removal from Surfaces

Certain areas of metal parts may have adhered pieces of epoxy that must be removed. The metal might be beryllium, nickel-copper alloy, nickel-based steel alloy, (stainless steel, 52100 bearing steel, or a variety of other special alloy steels). The surfaces include flats, internal and external cylinders, grooves, rim fillets, etc. This type of task was initially thought to be most suitable for laser cleaning because, generally, epoxy is partially transparent to the laser beam and the metals are fairly reflective. In our discussions with AGMC, it was brought out that the greatest benefit for such a process might be for complex or composite parts that cannot be put into solution because of potential damage to adjacent



2.2 Potting Compound Machining and Removal From Surfaces

A few of the metal parts had potting compound residue to be removed (as in the sealant for the gold connector on a rotor coil assembly part). This part also had P-37 potting compound in bulk to be machined (etched) to the base of cracks that require repair by backfilling with epoxy. This material was believed to have a different mode of material removal than that of the epoxy because of its possible stronger absorption of the laser beam.

2.3 Filter Plate Cleaning

In the discussions with AGMC, it was revealed that there was some difficulty getting good adhesion of a green glass filter plate to a CRT faceplate. In this case, the poor bond may have resulted from a contaminant film. This seemed to be appropriate for plasma cleaning, which is often used to get good adhesion of deposited metal films on glass.

2.4 Fill Fluid Residue Desorption

Another cleaning problem under consideration at AGMC was that of desorption of residual fill fluid that has come in contact with potting material because of an internal leak. The part is cleaned and then vacuum degassed for 2 days. Lasers or plasmas might be appropriate to speeding up the desorption process, depending on the nature of the surface, access, and degree of penetration (diffusion of the contaminate) into the surface.

2.5 Fine Particulate Removal

In the final assembly of parts in the rebuild process, residual particulates on the "clean" parts must be removed. These particulates range in size from submicron to tens of microns and may be organic or inorganic in nature. This cleaning is normally done in a clean room with a freon flush using filtered freon. Ionized dry filtered nitrogen is also used. Lasers can potentially remove particulates, but care must be taken to avoid redeposition in flowing gas systems.

3.0 Advanced Cleaning Technology Assessment

At the initiation of this project, several advanced cleaning techniques were envisioned that might be appropriate to precision guidance component cleaning. For completeness, a literature search was undertaken to assess the state of the art in advanced technology cleaning methods and to provide a point of departure for experimental research to demonstrate applicability of the leading candidate techniques. Results of this search are summarized below.

3.1 Literature Search Approach

The search terms used in the computer literature search are listed in Table 1 along with the qualifiers used to reduce the amount of information to a manageable size. More than twenty data bases were searched including Inspec, Spin, Energy Science & Technology, Aerospace, NSA, and NTIS, with dates going back more than thirty years to the present. The abstracts received from the search were analyzed for relevance and the most significant references were obtained in full hard copy form. These were examined and further reduced to those that were most relevant to the AGMC cleaning mission. Study of the citations in the key papers revealed additional literature that was then added to the collection. The most significant results gleaned from these papers are discussed below.

3.2 Plasma Cleaning

Plasma cleaning is one type of surface processing, among several, that depend on production of a low pressure steady-state plasma in a special vacuum chamber. These processes include sputter deposition, ion plating, plasma enhanced chemical vapor deposition, etching, cleaning, and surface modification. These techniques are fairly well developed and are used widely in industry. Plasma cleaning is, by its nature, a batch process and has a relatively low cleaning rate that is most appropriate to thin contaminant film removal. A recent review article by Coburn⁽¹⁾ presents a good basic overview of plasma surface processing and a guide to terminology used in the field.

Table 1. Literature search results.

Search	Key Words	Strategy	Hits
1	Laser? and Clean? and Remov? or Vaporiz? or Evaporate? or Ablat? or Strip	Title or Abstract	19,372
		Reviews Only	434
		Title	73*
2	Clean? and Glow discharge? or Plasma? or Microwave?	Title or Abstract	1,346
		Review Only	25*
3	Laser? and Clean? but not Search 1	Title or Abstract	3,098
		Title	166*
4	Laser? in Title and Clean? and Surface? in Abstract		136*
5	Laser? and Ablat? or Strip? in Title and Clean? in Abstract		17*

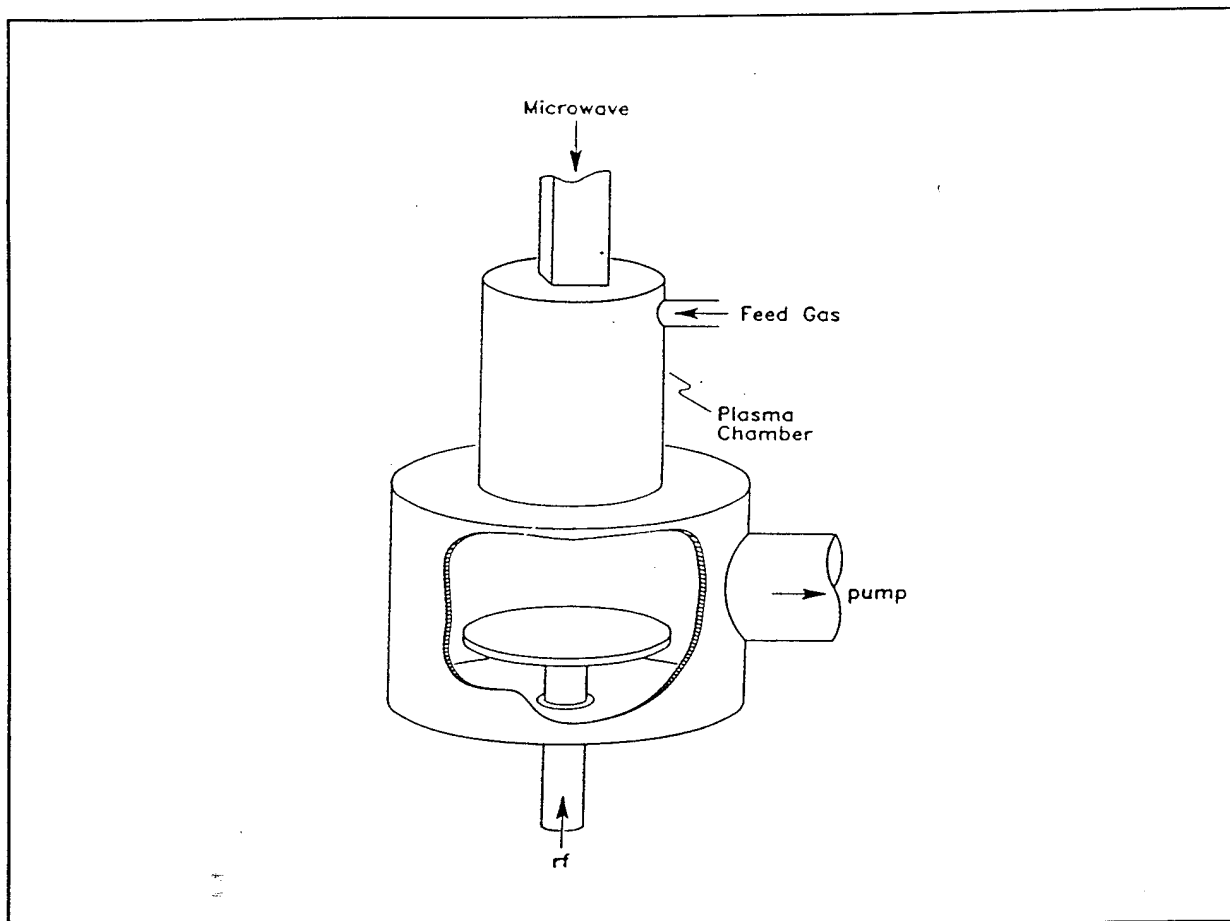


Figure 3. Microwave powered discharge geometry (Ref. 1).

based upon the substrate material (conductor, insulator, etc.) and the nature of the contaminant.

The mechanism of plasma cleaning is simply that which is generally used in plasma etching. If an inert gas is used, the ions and neutrals in the plasma bombard the surface to be cleaned and sputter off the contaminant film molecule by molecule, a purely physical process. By using a reactive gas in the plasma, the bombarding ions also may react with the contaminants and form gaseous species that evaporate from the surface. For energetic ions this process is known as reactive ion etching and is used in microfabrication as well as in cleaning. Examples of plasma cleaning processes found in the literature are discussed in the following paragraphs.

3.2.1 Plasma Cleaning of Metals

Bearing Surface. As early as 1968, plasma cleaning was found to be effective in guidance system component cleaning.⁽²⁾ Galvin, et.al., reported an investigation of the effectiveness of glow discharge cleaning of gas-bearing gyros. They were interested in increasing the adhesion of a lubricating film to the gyro's shaft and rotor. This can be accomplished by furnishing a clean surface to the lubricant. The main alternative to glow discharge cleaning of a gyro surface was to employ organic solvent, detergent, and water baths followed by a light abrasive buffing to prepare bearing surfaces for the lubricant. This was found to be a time consuming process; days were involved. By contrast, glow discharge cleaning was on the order of minutes. In the cleaning tests, an Argon plasma produced in an industrial plasma cleaner was used. Typically, the contamination layer to be removed was only 1-3 molecules in depth. The efficiency of removal was judged by using two techniques. The first technique measured the increase in the magnitude of the coefficient of friction of the cleaned surface as a function of time. An increase in friction was assumed to be associated with a decrease in the number of contaminants on the surface. The coefficient of friction increased by a factor of 1.7 with 15 minutes of cleaning. A better test that was used involved the contamination of the gyro surface with a radioactive stearic acid. Initially, 1000 counts per minute were measured, but after 10 minutes of glow discharge cleaning, this rate was reduced to 10 counts per minute.

Deposition Preparation. O'Kane and Mittal⁽³⁾ report comparison of traditional solvent cleaning with RF plasma cleaning for preparing rhodium and iron-cobalt surfaces to receive a vapor deposited polymer film. They used water wettability and Auger electron spectroscopy to measure the cleanliness of the surfaces. Their results showed that argon or helium-oxygen plasma cleaning was more effective than solvent cleaning in removal of sulfur and carbon contamination. No damage to the magnetic properties of the surface was observed.

In another study motivated by the need to get good adhesion and interface bonding in depositions (in this case an aluminum deposition), Kominiak and Mattox⁽⁴⁾ found that a reactive plasma cleaning was most effective for their titanium, 304-stainless steel, Kovar, and nickel-cobalt steel substrates. Using soft x-ray appearance potential spectroscopy to check

cleanliness, they obtained the best results in carbon residue reduction with low voltage RF sputtering (300 V) with an Ar-HCl mixture forming the plasma.

Baker⁽⁵⁾ studied the reactive plasma cleaning of copper, aluminum alloy, and Inconel 625 with DC and RF discharges in argon-oxygen mixtures. He used a mass spectrometer set on CO₂ to monitor carbon evolution from the surface and calibrated the measurement by etching a pure carbon film. Baker found that reactive plasma cleaning was most effective at removing the deeply bonded carbon when the workpiece was at cathode potential to enhance the ion impact energy.

Perhaps the most relevant work found was that of Ward and Buss⁽⁶⁾ who recently studied plasma cleaning as a waste minimization tool with goals similar to those of AGMC. They experimentally investigated the effect of the process parameters on the plasma removal of thin films (1.5-7 μm) of PMMA and poly-2-vinylpyridine from a substrate located in a research chamber using parallel plate electrodes with RF excitation. They found that by using a 40% SF₆/O₂ plasma, that had an optimized plasma pressure (250 Torr) and power density, a removal rate of approximately 5 nm/sec (19 $\mu\text{m/hr}$) for PMMA could be obtained. This was an enhancement of two orders of magnitude over the removal rates of commercial plasma cleaners. By contrast, an optimized argon plasma only produced a removal rate of 0.08 nm/s.

Additional experiments addressed the removal of A-9 aluminum cutting fluid oil from substrates. The A-9 was a mixture of hydrocarbon solvents, waxes, fatty acids, fragrances, and dyes. In their report they did not state the amount of oil that was present in the substrates that were tested. Using a 40% SF₆/O₂ plasma they were able to obtain a removal rate of 7.5 nm/s. Further results are shown in Table 2.

Table 2. Contaminant film removal rates for RF plasma cleaning.

Material	Removal Rate (nm/s)	Gas
PMMA	0.6	oxygen
poly-2-vinylpyridine	0.4	oxygen
PMMA	0.08	argon
PMMA	5.0	SF ₆ /O ₂
A-9 Machine oil	0.5	O ₂
A-9 Machine oil	7.5	SF ₆ /2

The slow rate of plasma removal (7 nm/s) even with optimized conditions indicates that only thin films could be removed from a surface in a reasonable time. For example, at a plasma removal rate of 7 nm/s it would take 4 hours to remove a 0.1 mm thick contaminant layer from a substrate surface.

3.2.2 Plasma Cleaning of Circuit Components

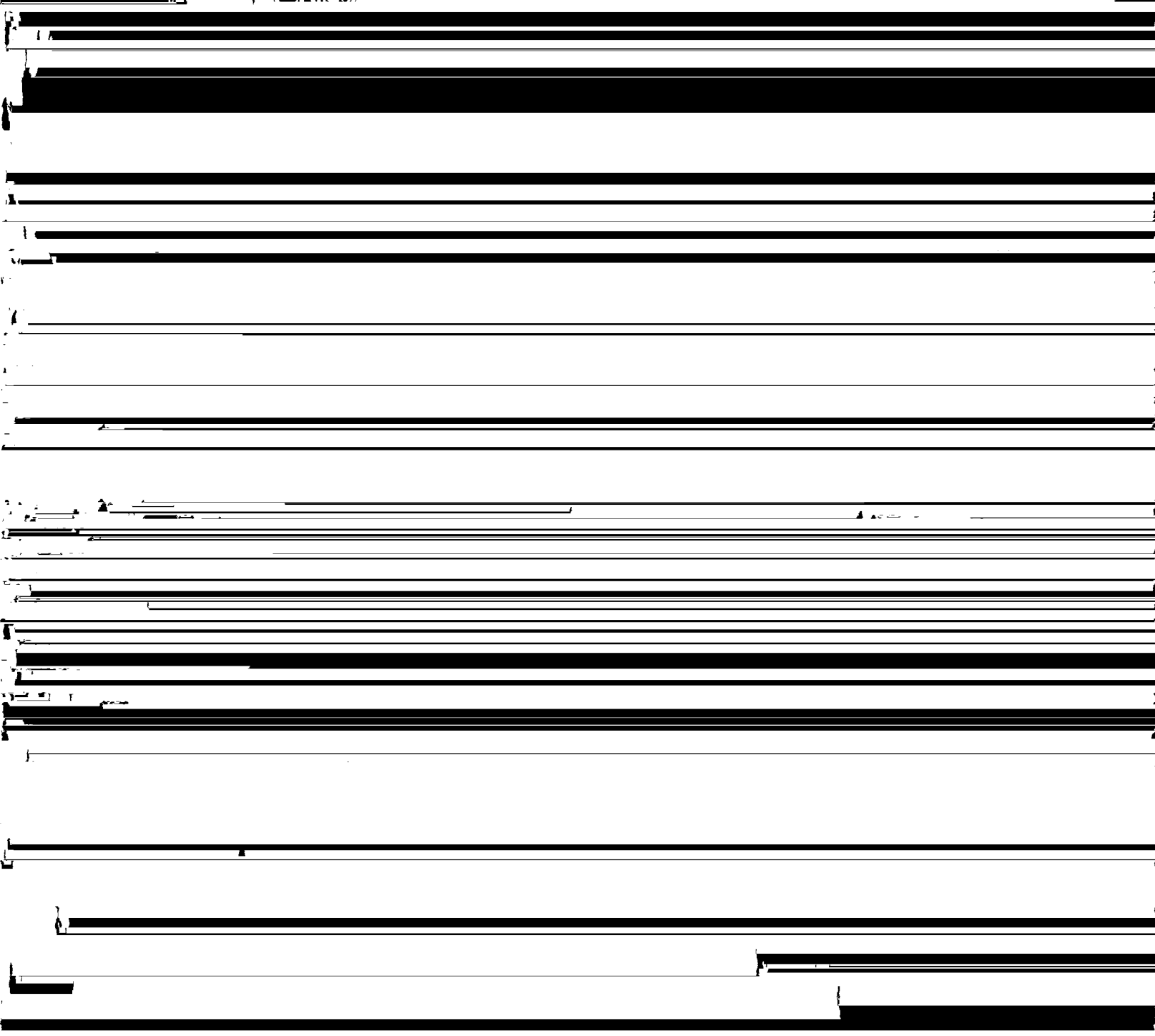
Several papers were found that indicate that plasma cleaning can be of value in cleaning circuit boards. IBM researchers^(7,8,9) discovered that RF reactive cleaning with oxygen-carbon tetrafluoride may be used to remove epoxy/glass particle/copper drill smears in drilled through holes in printed circuit boards. Nonreactive and reactive plasma cleaning have also been studied for preparing hybrid integrated circuits prior to wire bonding.^(10,11,12,13) Performance exceeding that of standard solvent cleaning in removing adhesive vapor residues has been achieved as measured in terms of wire bond yields.

3.2.3 Other Plasma Cleaning Applications

Other plasma cleaning applications of less relevance to AGMC include cleaning of high vacuum systems (such as accelerators and fusion research chambers) and vacuum devices for the purpose of achieving and maintaining high vacuum levels.⁽¹⁴⁾ Plasma discharges have also been used for cleaning x-ray optics⁽¹⁵⁾ and preparing semiconductor surfaces for depositions and device manufacture.^(16,17)

3.2.4 Plasma Cleaning Conclusions

Based on this survey it was found that the plasma cleaning process was fairly well developed and commercialized, but that the cleaning applications were limited in scope. By its nature, plasma cleaning has very low rates of contaminant material removal and cannot, therefore, be used effectively for removal of bulk contaminants such as epoxy patches or



There are several notable advantages of laser cleaning:

- the process is generally very fast and energy efficient,
- the area to be cleaned can be highly selective and sharply defined,
- no foreign atoms are introduced to the surface as in ion bombardment techniques,
- if cleaning is done in vacuum, the vacuum is not compromised because the laser source can be located outside of the cleaning chamber,
- thermal diffusion of bulk impurities to the surface is avoided because of the extremely large quenching rate afforded by very short pulses available,
- the removal rate can be easily controlled by changing the beam fluence or pulse repetition rate.

The following sections outline specific techniques and applications for laser cleaning.

3.3.1 Laser Cleaning of Metal Surfaces

There are at least two mechanisms in laser cleaning of metal surfaces: laser ablation of absorbing contaminants and laser driven blow-off of transparent contaminants. Laser ablation is the vaporization of thin layers of contaminants at the air-contaminant interface. Efficient use of this mechanism requires that the contaminant be strongly absorbing at the laser wavelength. Typically, in the absence of a strong absorption peak, far UV wavelengths are preferred because broadband absorption occurs in most materials in this wavelength region. Also, more efficient contaminant removal is found for short pulse-width, high peak-power lasers.

The blow-off mechanisms occur when the material is mostly transparent to the laser beam, which passes through the contaminant and initiates a microexplosion at a subsurface site, either at small absorbers within the contaminant or at the metal surface. The trapped expanding vapors generated from the microexplosion pop off relatively large pieces of contaminants. This mechanism is, in general, more efficient than ablation because less energy goes into the heat of vaporization to remove the same mass of material. The cleaning

process is self-limiting at laser wavelengths that are reflected by the metal surface, provided that the beam fluence is below the damage threshold of the substrate. Self-limiting behavior has been observed by Peebles⁽²¹⁾ using a YAG laser to clean oxide from SS-304, but the limiting behavior should be dependent only upon the reflectivity of the substrate to the laser wavelength and is generally applicable.

The most common contaminant found in the literature are oxide films which have been effectively removed using a pulsed YAG laser. This can be used to advantage in reducing chemical usage in processes such as fluxless soldering.⁽²²⁾ The threshold for efficient film removal varies only slightly with film composition, but is typically about 1 J/cm² in all cases reviewed. Laser cleaning is typically done in a cleaning chamber that is either evacuated or pressurized with an inert gas like helium or argon, with the laser beam introduced through a window. However, it is feasible to perform cleaning in a clean room with a fume hood and a flowing inert gas.

No data on laser removal of epoxy films or patches were found in the literature.

3.3.2 Laser Cleaning of Non-Metal Surfaces

The bulk of literature on laser cleaning of non-metal surfaces has been directed toward the cleaning of semiconductor materials. However, some literature, which was not reviewed in detail, was directed toward cleaning stone statuary and painted art work. The primary semiconductor contaminants that have been laser cleaned are oxide films and absorbed metal ions. Over the past 25 years, ruby, Nd:YAG, alexandrite, and CO₂ lasers have been used for cleaning, but more recently, excimer lasers have been the focus of most laser cleaning of

The optimum cleaning fluence for oxide removal via excimer lasers was found to be very similar to that identified for film removal from metal substrates, i.e., 1 J/cm² to 1.3 J/cm², which is typically enough intensity to remove a thin oxide film with a single pulse. Material removal, however, has been observed at very low beam fluences, as low as 20 mJ/cm², but these low beam fluences require hundreds of pulses to remove a thin film. Typical rates of removal are in the tens of nanometers per Joule per square centimeter. As with metal substrates, most of the laser cleaning of semiconductor substrates has been conducted in a vacuum chamber or a controlled inert background gas.

3.3.3 Liquid Assisted Laser Cleaning

Many of the AGMC repair and maintenance tasks require final cleaning of the surfaces in a clean room environment using methods that achieve very low numbers of residual particles on the part surface. These micron-size particles are extremely difficult to remove because the binding forces (Van der Waals, capillary, and electrostatic) holding them on the surface are much greater than gravitational and inertial forces at this particle size. Traditionally, a filtered Freon wash performed in a laminar flow clean station is used for this step. A similar problem arises in semiconductor device microfabrication, where micron-size particles cause defects on the same scale as that of the microstructure being produced in the process. Two groups have developed liquid assisted laser cleaning techniques that have successfully achieved particulate removal without Freon or harsh solvents. It is important to note that the liquid that is used does not reside on the surface for longer than a second or so.

Zapka and colleagues at IBM^(25,26,27,28,29) have developed a technique wherein a very thin volatile liquid layer (water, ethanol, methanol, isopropanol, and mixtures thereof) is formed on the surface to be cleaned just before delivery of a short laser pulse. The liquid works its way under the particles by capillary action and is explosively evaporated by conduction of heat from the substrate which is heated directly by the laser pulse. They conducted most of their research on silicon surfaces exposed to 16-ns laser pulses from a KrF excimer laser (0.248 μm wavelength). Their best results were obtained using an 80/20 water/methanol solution to produce a vapor that was puffed onto the surface about 100 ms prior to firing the laser. Particles of gold, silica, alumina, and latex with sizes in the 0.1 to

10 μm range were effectively removed with laser pulse fluences in the 30-300 mJ/cm^2 range. The IBM researchers consider the process a dry cleaning process because of the short residence time of the liquid on the surface.

In similar work at the University of Iowa, Allen and colleagues^(30,31,32,33,34.) have cleaned micron and submicron size particles from silicon substrates using a slightly different approach. In their work they use a laser wavelength that is absorbed directly in the liquid

been used in an attempt to clean a glass surface.⁽³⁶⁾ However, the longer pulse width resulted in a larger heat deposition and substrate crazing. Cleaning thresholds depend on film composition and laser wavelength, but are typically in the 100 mJ/cm^2 to 500 mJ/cm^2

4.0 Experimental Validation of Laser Cleaning Technology

After consideration of the advanced cleaning technology assessment and review of the specific candidate cleaning tasks identified jointly with AGMC, it was concluded that experimental validation should proceed on laser epoxy removal, potting compound machining/removal, and fine particulate removal. Although no data on removal of epoxy from metals with lasers had been found, several interaction mechanisms were believed to be viable for its implementation. In light of this potential and the high leverage it would provide AGMC in solvent-use reduction, a major effort was made to prove this technique. The potting compound was likely to be etched cleanly at excimer wavelengths ($0.25\ \mu\text{m}$), but no data were available for other wavelengths of interest and potting compound studies were planned and carried out along with the epoxy removal studies. Finally, there was clear evidence that particulate contaminants could be cleanly removed from silicon substrates with an excimer laser. Research was undertaken to demonstrate this process for steel substrates and longer wavelengths.

The following sections summarize the research conducted in these three cleaning task areas.

4.1 Epoxy Removal

Prior Battelle experience on laser interaction with epoxies suggested that several mechanisms may be available for accomplishing a wide variety of location specific epoxy removal tasks. In particular, the laser offers the potential for cleaning composite (or complex) parts where certain susceptible areas on the part to be cleaned must remain unaffected by the cleaning process (precluding soaking, for example). Cleaning mechanisms and experimental research undertaken to demonstrate epoxy removal from metal surfaces are discussed below.

4.1.1 Laser Interaction Mechanisms for Epoxy

Most epoxies have some transparency to visible and near IR laser light, which offers the possibility for the following mechanisms:

- Defect site and low-level absorption initiated nonlinear absorption in the epoxy (thermal expansion or gas initiated blow-off of epoxy),
- Metal substrate heating (differential thermal expansion, volatilization of epoxy constituents by conduction),
- Explosive heating of liquid introduced by capillary action at the edge of the epoxy patch,
- Self-enhancement of all of the above effects by multiple exposures (absorption sites in the epoxy grow with time, mechanical strength degrades, interfacial cracks enlarge).

Some of these mechanisms are illustrated in Figure 4. Even neat epoxies have small defects that serve as absorption site initiators when the fluence is sufficiently high. The presence of fillers in some of the structural epoxies of interest to AGMC suggested that this site density might be high and dominate the interaction. In such a case, the absorption site initiates a pyrolysis reaction which further enhances the absorption via the presence of carbon. The pyrolysis gas pressure fractures the epoxy and crack growth ultimately leads to blow-off of chunks of epoxy. This mechanism of material removal was observed in the tests at the higher laser pulse fluences, but it turns out that for the conditions investigated, a debonding of the epoxy at the epoxy/substrate interface was observed at lower fluences. This debonding is a new result and the mechanism is not yet known with certainty. It is speculated that the substrate absorbs most of the heat and expands faster than the epoxy. The shear stress may then be responsible for the debonding effect. A third mechanism is illustrated in the right hand portion of Figure 4. It was suggested at the beginning of the program, that if slight debonding could be achieved near the edge of an epoxy patch, liquid introduced by capillary action could be explosively heated by the laser and effect patch removal through crack growth at the interface. This mechanism was not investigated extensively because it was found that a single pulse could remove an epoxy patch without a

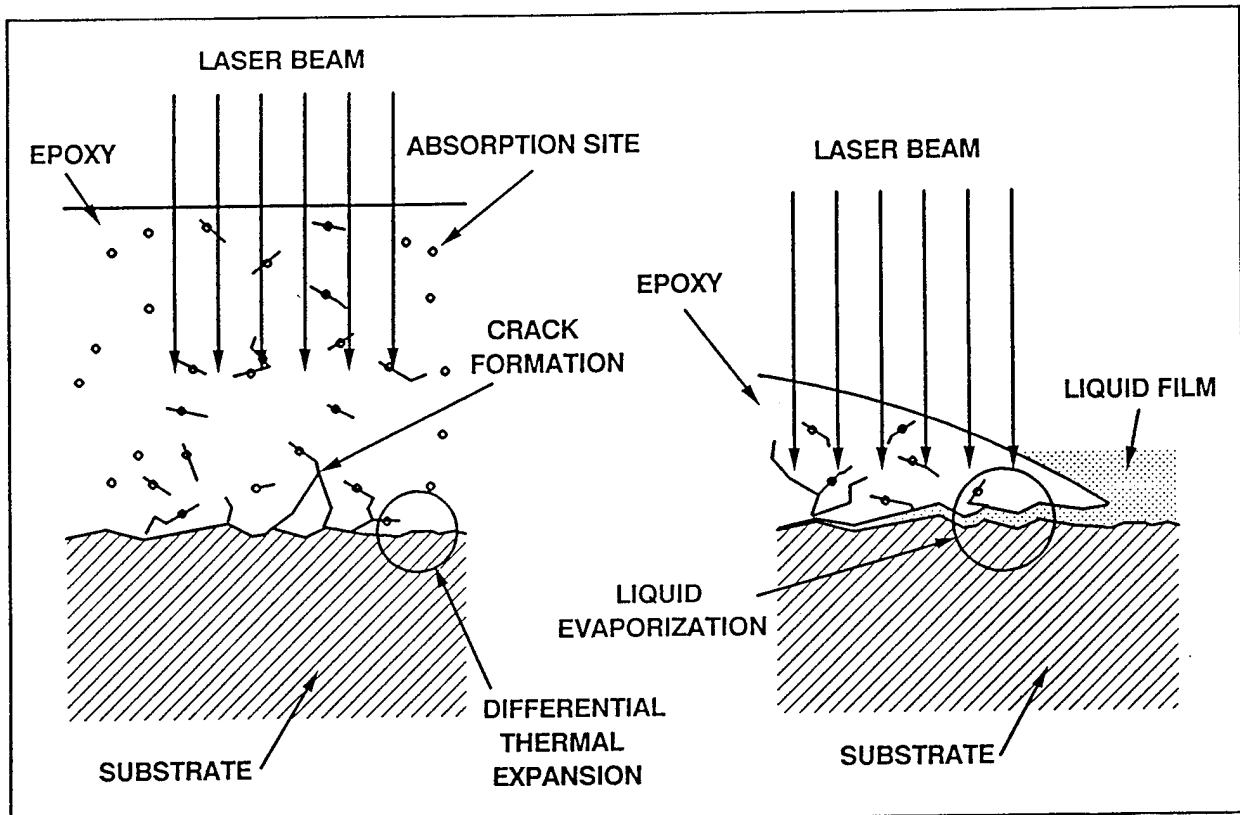


Figure 4. Possible mechanisms of visible/IR lasers with epoxy materials.

liquid assist. Once the debonding was discovered, most effort was devoted to measuring its threshold and the threshold for marking the substrate.

4.1.2 Epoxy Sample Preparation

While a limited number of real parts with epoxy patches were available for demonstrations, the number of tests anticipated for the research and the need for uniform results required that steel substrates be prepared with epoxy patches adhered to them. The

kits. All resins were cured with No. BA-5 activator. The epoxy resin/activator mixtures were vacuum degassed, cast, and cured for 1 hour at 200 F in all cases.

Epoxy layers of 0.005, 0.010, and 0.030 in. (125, 250, 750 μm) were cast on the SS-304 plates by the above techniques. In most cases, the epoxy that squeezed out under the teflon dam provided an additional layer with which to experiment. This layer was typically in the 0.001-0.003 in. (25-75 μm) range and was representative of the thickness in some actual part cleaning tasks. Some free form patches of epoxy or "dabs" were also formed on the steel substrates to represent the geometry of screw staking patches. These were rounded somewhat by surface tension and were irregular in size and shape. Generally, they were much larger than the screw staking patches (1-5 mm diameter, 0.3-1 mm thick).

4.1.3 Experimental Apparatus and Approach

The epoxy removal trials were initially performed with a Continuum Model 481C-S Nd:YAG laser operated in the fundamental, second harmonic, and third harmonic modes to provide 1.06, 0.53, and 0.355 μm wavelengths, respectively. The laser has an injection-seeded Q-switched mode of operation that provides 8-10 ns pulses (FWHM). The experimental arrangement is shown schematically in Figure 5. The beam was delivered to the target through a 4 mm circular hard aperture and 1:1 imaging relay optics. This permitted selection of a spatially uniform portion of the beam and precise definition of a circular uniform irradiance area on the target surface. Uniformity $\pm 10\%$ from the flat-top average fluence was confirmed with a silicon array camera (as shown in the figure). The beam energy on target was controlled by placing filter glass attenuators in the beam before the 4 mm aperture. A beam splitter was used to sample the beam on each pulse for energy measurement with a Laser Precision Model RjP-734 pyroelectric probe. This probe and the sampling train were calibrated with a second calorimeter placed at the target position. A Hamamatsu Model R1328U-01 vacuum photodiode was used to measure the temporal pulse shape.

The stainless steel substrates were held in a translation stage fixture inside a plexiglas environmental chamber that permitted placement of multiple exposure areas on each substrate. A HEPA filter was added to the exhaust duct for beryllium exposures. In the

epoxy was found to be about 0.3 J/cm^2 . The mark was dark gray, indicating that internal pyrolysis and carbon formation had occurred. No mass loss was observed at this level, however, even if the pulses were repetitively delivered to the same spot. The fluence was raised to higher levels to assess the threshold for mass loss by the blow-off mechanism. Figure 6 presents results of these measurements for the LCA-9/BA-5 epoxy. Trains of pulses delivered at 5 Hz and having various train durations were used to construct the curves. Mass loss was measured for each train duration (plotted in terms of numbers of pulses in the train). For 0.8 J/cm^2 per pulse, no mass loss was detected (points are shown at the noise level of mass loss detection), but at 1.27 J/cm^2 per pulse, mass loss was clearly evident and a crater appeared. Based on these tests, the threshold for LCA-9/BA-5 epoxy blow-off for this material appears to be about 1.0 J/cm^2 per pulse at the 10 ns pulse width. Unfortunately, this threshold is fairly high and the SS-304 exhibits minute amounts of surface melting (micromelt) at this fluence level which may cause some concern (although it is mostly a cosmetic change).

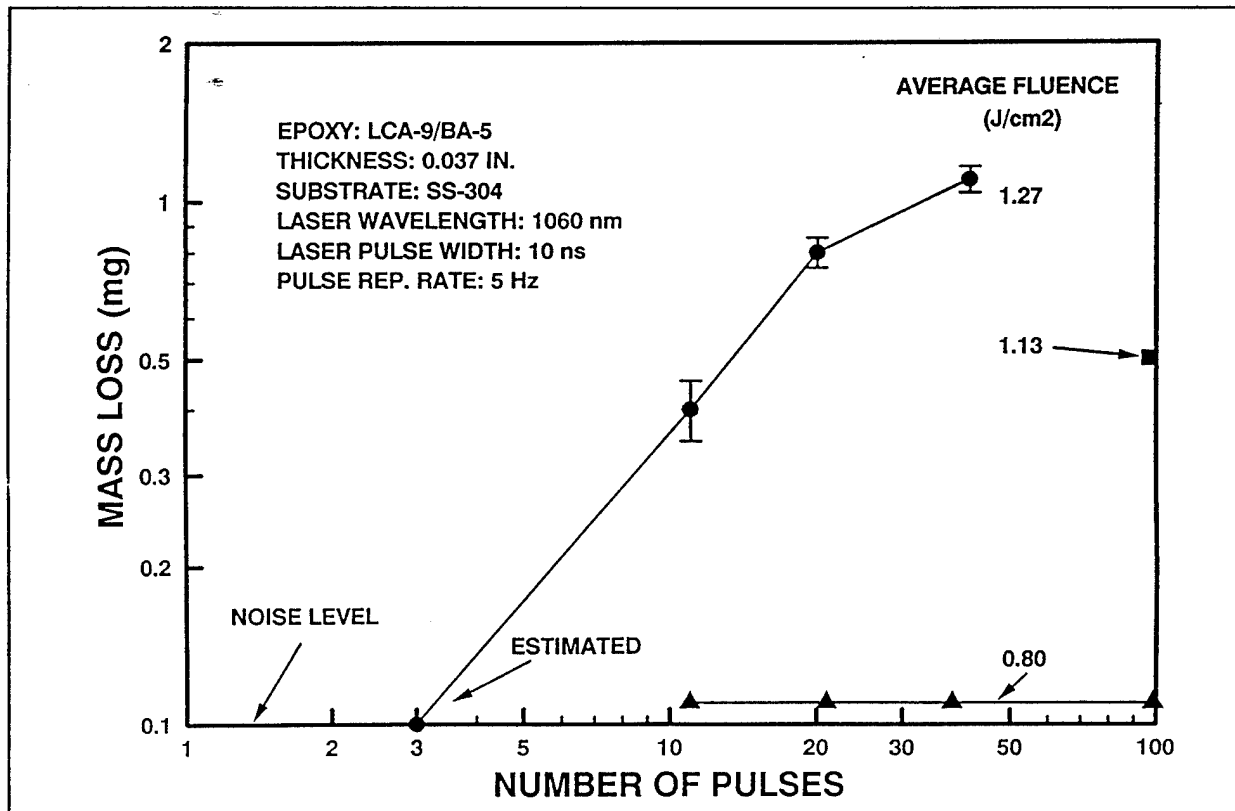


Figure 6. Mass loss behavior for laser exposure of a thick epoxy layer.

During these tests, it was observed that exposure of the thin layer of epoxy surrounding the thick cast region exhibited clear debonding from the substrate under the circular exposure area in a single pulse. This result was very significant because it confirmed the possibility of removing epoxy with no effluent vapor generation. The debonding process was then made the focus of the remaining epoxy removal experiments. Samples of each of the three epoxies with thicknesses in the 0.007-0.011 in. range were exposed in a series of single pulse tests to determine debonding thresholds. These thresholds were found to be about 0.2 J/cm^2 for the 10 ns, $1.06 \mu\text{m}$ laser pulse. Some change in surface appearance of the substrate was noted in the tests and a series of exposures of the bare substrate was performed to explore thresholds for marking. Based on microscopic surface examination, it appeared that some micro-melting (smoothing of rough surface features and scratches) occurred at 0.8 J/cm^2 . At lower fluence, the slight marking is believed to be oxide removal and cleanup of loosely attached metallic features on the surface that cannot conduct heat to the substrate. While these changes in the substrate surface are believed to be cosmetic in nature, subsequent tests included checks of the substrate marking

Before proceeding with additional tests, the feasibility of removal of large areas of epoxy by laser debonding was confirmed in repetitive pulse tests. A SS-304 substrate with a 1 in. diameter (0.010 in thick) epoxy layer was hand-held in the beam which pulsed at 5 Hz with a 0.36 J/cm^2 per pulse fluence on the surface. The hand scanning of the part under the 4 mm diameter beam was far from optimum, but the layer was removed in about 1200 pulses (<4 minutes). Later research showed that the considerable scan overlap in this test was not required. A video tape of this demonstration is available. The substrate exhibited only slight marking, probably oxide removal.

A demonstration was also performed with mm-size epoxy patches on 52100 bearing steel substrates provided by AGMC. The epoxy patches were made from the LCA-4 resin as described above. Several single pulse tests were conducted with the patches. In those cases where the irradiance area covered the patch completely, the patch would often jump completely off the surface in one pulse. Sometimes light scribe force was used to overcome the electrostatic force holding the debonded patch on the surface. Patches debonded typically at 0.21 J/cm^2 and jumped off the surface at 0.25 J/cm^2 . A video tape of this demonstration is available.

Because marking of substrates (believed to be cosmetic) occurred near the debonding thresholds, longer laser pulses that might provide a larger margin between the debonding threshold and the substrate marking threshold were investigated. These tests were conducted at 150 ns and 1 ms because of the availability of custom-built lasers at Battelle with these characteristics. At 150 ns the ratio of marking threshold to debonding threshold increased significantly and at 1 ms the ratio is believed to be even higher. The significant result is that the debonding threshold rose slower with increasing pulse width than did the marking threshold.

For short pulses where the conduction of heat into the metal during the pulse is quite shallow in depth, the heating of the surface may be simply modeled. The gaussian temporal profile of the laser pulse can be approximated by a triangular pulse having the same pulse

width at half maximum power. The temperature at the surface of the substrate is given by

where F_p is pulse fluence, α is surface absorptance, k is thermal conductivity, ρ is density, c_p is specific heat, and t_p is pulse width. Substituting SS-304 properties and setting ΔT equal to the melt temperature, the threshold melt fluence can be calculated as

$$F_p \approx 4700 t_p^{1/2}$$

This result is very approximate, but shows the well-known temporal dependence for the melt threshold on a surface. Figure 7 displays this result as a dashed line along with the measured marking threshold points (squares) and the debonding threshold data (circles). The agreement of melt theory with the marking threshold for short pulses is reasonable. Melt is not observed on the samples at the marking threshold because of the extremely short duration of any melt condition that may have occurred and the shallow heating depth ($0.2 \mu\text{m}$ at 10 ns and $0.7 \mu\text{m}$ at 150 ns). At 1 ms , the melt model should predict the threshold fairly well because there is time for metal to flow. Measurement of melt threshold at 1 ms was beyond the fluence level available in the setup at the time of the tests, but the model and the

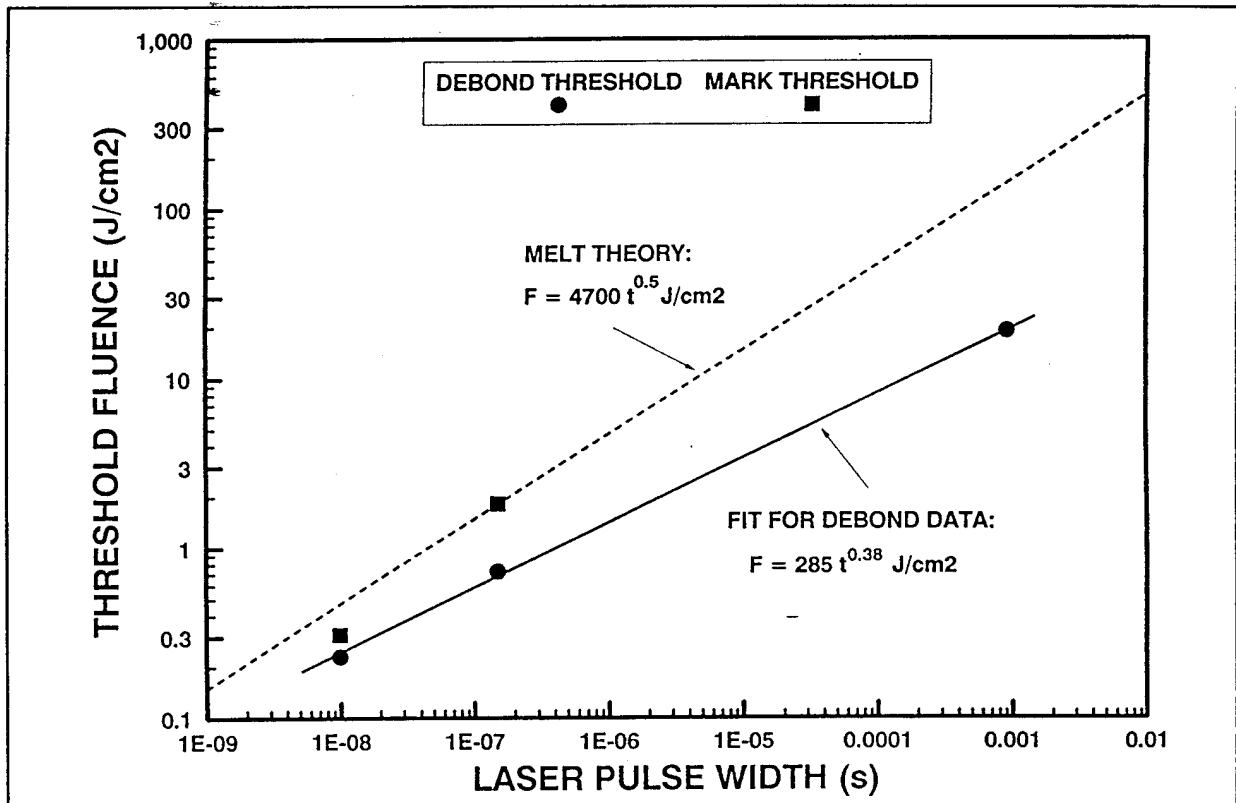


Figure 7. Single pulse thresholds for epoxy debonding from stainless steel substrates.

debonding data suggest that debonding occurs at a fluence level more than a factor of 7 lower than that for melting at this pulse width. The temperature rise at the surface is no more than about 200 C and the depth of penetration of the heat is about 60 μm . The slower dependence of debonding threshold on pulse width ($t^{0.38}$) is likely due to the thermal expansion depending on depth of the thermal profile as well as the magnitude of surface temperature.

Another variable investigated in the epoxy removal research was the effect of the laser wavelength on the removal process. Second and third harmonics were available from the laser which permitted study of effects at 0.53 and 0.355 μm , respectively. Results of these tests are shown in Table 4. The thresholds were determined with uniform epoxy layers in the 0.005-0.010 in. range on SS-304 substrates except for the one point at 0.355 μm . The threshold was determined as that fluence at which about half of the area under the uniform irradiance area was debonded. No significant difference was noted between the 1.06 and 0.53 μm debonding results and all three epoxies behaved essentially the same. The threshold for micromelt of the SS-304 substrate surface dropped, however, for the 0.53 μm case. A uniform irradiance area was not achieved with the 0.355 μm beam and only the 52100 steel with isolated epoxy patches was tested. The patches could be removed, but the fluence was close to the micromelt threshold. It was concluded that the 1.06 μm wavelength was superior for epoxy removal because of the higher margin from the micromelt condition and the simpler laser apparatus that would be required.

Table 4. Summary of wavelength effect on epoxy removal thresholds (8-10 ns pulses).

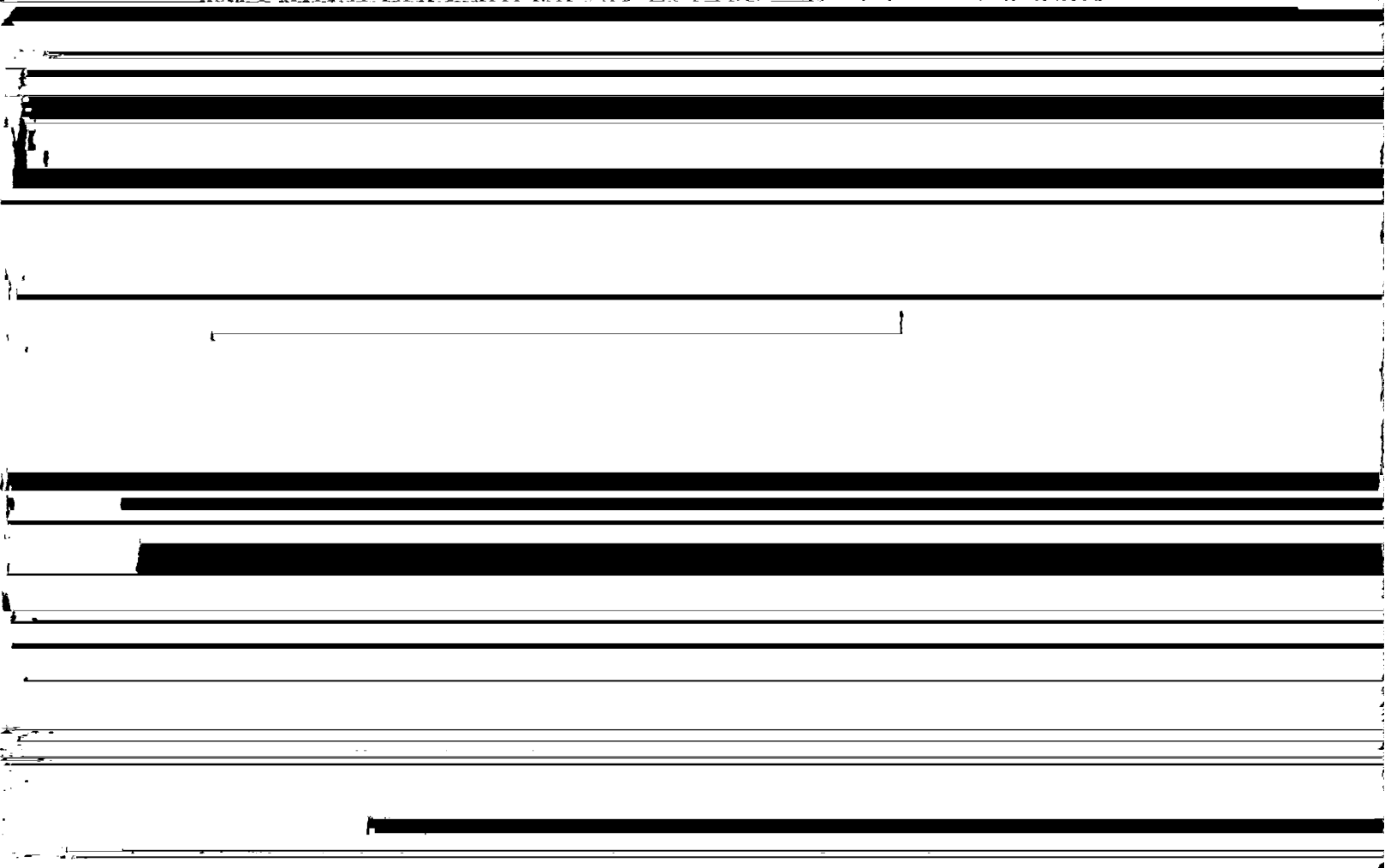
Material	Effect	Threshold Fluence (J/cm^2)		
		$\lambda = 1.06 \mu\text{m}$	$\lambda = 0.53 \mu\text{m}$	$\lambda = 0.355 \mu\text{m}$
LCA9/BA5	debonding	0.23	0.23	—
LCA4/BA5	debonding	0.23	0.22	~0.31*
FA8/BA5	debonding	0.22	0.23	—
SS-304	micromelt	0.85	0.47	~0.46
*52100 Steel substrate.				

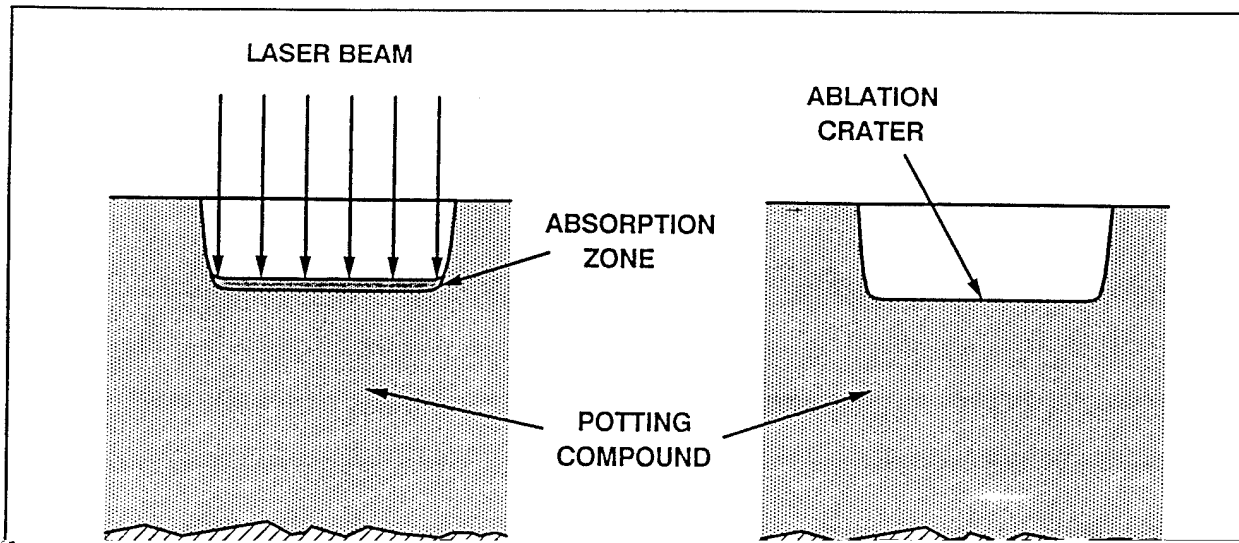
4.2 Potting Compound Machining/Removal

Potting compounds are typically used in the gyro components to contain electrical wires and connections such as the driver coils in a motor drive. In some cases a crack develops in service which must be machined or cut out and ultimately backfilled with repair epoxy. In other cases, the compound must simply be removed from a surface. The potting compounds differ from the epoxies primarily in the filler which was originally believed to be sufficiently absorbing to lead to an ablative-like behavior. This turned out not be the case in our experiments as discussed below.

4.2.1 Laser Interaction Mechanisms for Potting Compounds

As the absorption site density in a semi-transparent material such as epoxy is increased, the absorption length for the light becomes very short and ablative behavior ensues





will work for removing this material from metal but layer samples were not available for study.

4.3 Particulate Contaminant Removal

Experiments were undertaken to demonstrate the applicability of the liquid assisted laser particle removal as a final cleanup step that might replace the filtered freon wash in current cleaning procedures at AGMC. These tests extended the earlier IBM work to steel substrates and the $1.06\text{ }\mu\text{m}$ wavelength.

4.3.1 Laser Interaction Mechanisms

The mechanism employed to remove particles from a surface with a non-absorbing liquid is illustrated schematically in Figure 9. A very thin ($<50\text{ }\mu\text{m}$) transient liquid film is

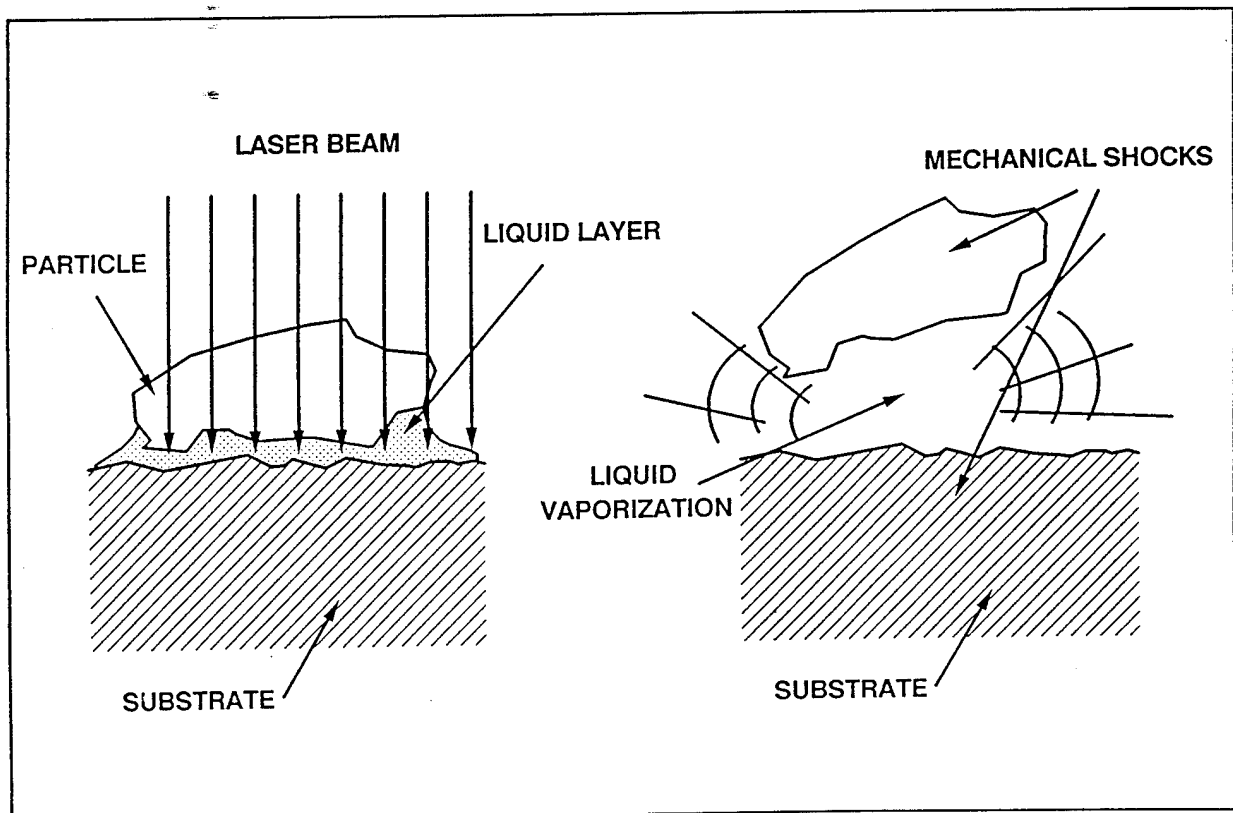


Figure 9. Mechanisms for removal of micron and submicron particles from a surface.

deposited on the surface to be cleaned just before the laser pulse is delivered (0.1-1 s). Some liquid is pulled under each particle by capillary forces. This liquid is explosively vaporized by heat conducted from the absorbing substrate and the particle is ejected from the surface. This is a relatively dry process since the film evaporates in less than a few seconds and employs benign liquids such as water or simple alcohols.

4.3.2 Sample Preparation

Two types of samples were used in these tests: 304 stainless steel (rolled finish) and 52100 bearing steel gyro parts. All samples were cleaned by washing the test surface with ethanol to remove most contaminants. Droplets of filtered ethanol containing silica particles were then deposited on the clean sample surface. After the ethanol completely evaporated, the silica particles remained on the surface of the sample. The average particle size was measured to be $0.8\text{ }\mu\text{m}$, with the largest particles in excess of $15\text{ }\mu\text{m}$.

After a sample was secured into the test fixture, it was exposed to a blast of high pressure canned air to remove any loose particles. This was done to ensure that the observed particulate removal was indeed due to the laser vaporization of the liquid and not due to the blast of vapor prior to laser exposure.

4.3.3 Experimental Arrangement

The experimental arrangement was identical to that shown in Figure 5, except that the test chamber was modified as shown in Figure 10. The laser beam was changed to 45° incidence to permit clear viewing of the particles. A video camera with microscope optics having a measured $2\text{ }\mu\text{m}$ resolution was positioned normal to the surface to look at the residual particles on the surface at the center of the laser irradiance area. Although the measured resolution of the camera is approximately $2\text{ }\mu\text{m}$, sub-micron particles can be detected by shining a high intensity light at a glancing angle to the substrate surface to provide dark field illumination. While particle size cannot be accurately determined, submicron particles can be detected as a bright spot or pixel on the video monitor. The video output of the camera was recorded on 3/4 in. video tape for post-test analysis.

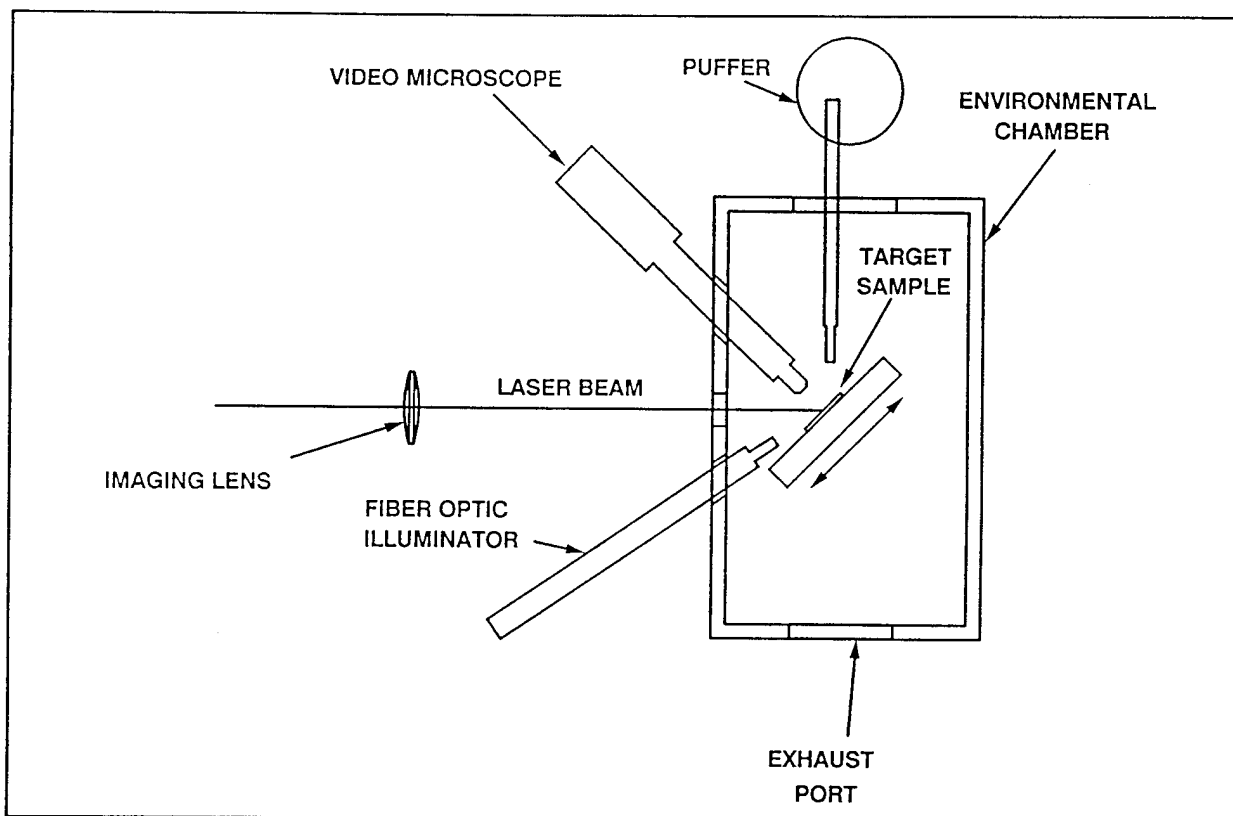
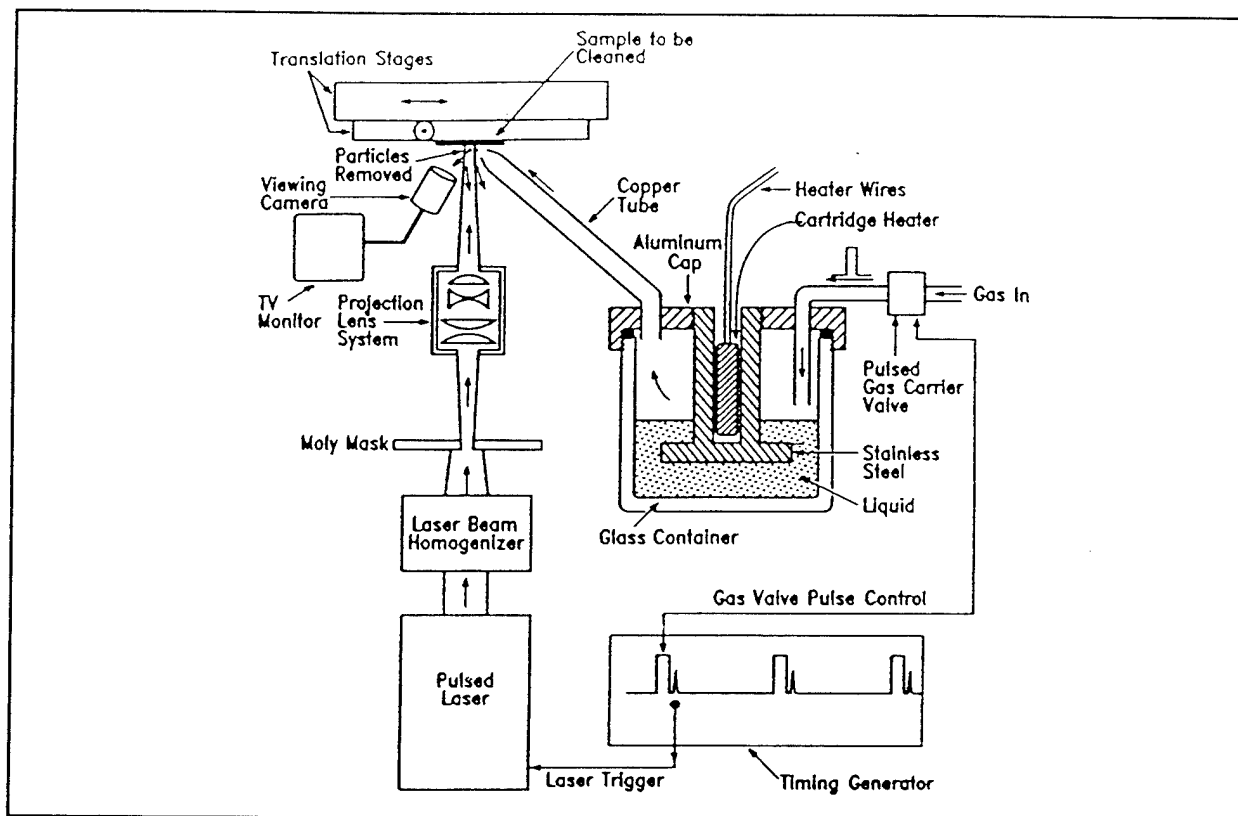


Figure 10. Modified experimental arrangement for laser particulate removal demonstration.

A saturated vapor "puffer" was designed and fabricated to apply a thin liquid layer to the sample surface just prior to laser irradiation. This device followed closely the device design used by Tam, et.al.⁽²⁸⁾ in their research as illustrated in Figure 11. The vapor delivery device was constructed from a pyrex tube 90 mm long with 7.2 mm thick walls and a 10 mm thick bottom. The top lip of the container was ground to provide an O-ring seal for pressurizing the container. The top cap was a 10 mm thick x 125 mm diameter piece of stainless steel with an O-ring groove. An 18 mm diameter stem supported a heat distribution disk which was 10 mm thick and 75 mm in diameter. This disk, which was 61 mm below the top cap, was one integral piece with the stem. A bottom plate which was also 125 mm in diameter, held 3 threaded rods which passed through the top plate. Nuts tightened the top plate against the O-ring and container providing a pressure tight cell. The 18 mm stem was bored out to hold an 85 W, 115 Volt cartridge heater. Its purpose was to heat the water-alcohol mixture to 40 C to generate vapor in the space above the liquid. The cell was normally about 1/2 full of liquid.

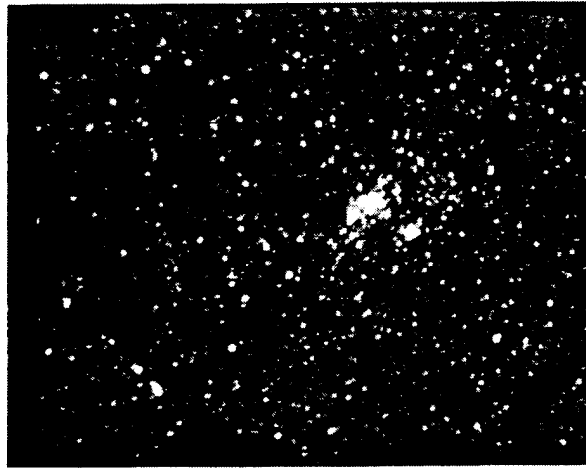


particulate (Ref. 28).

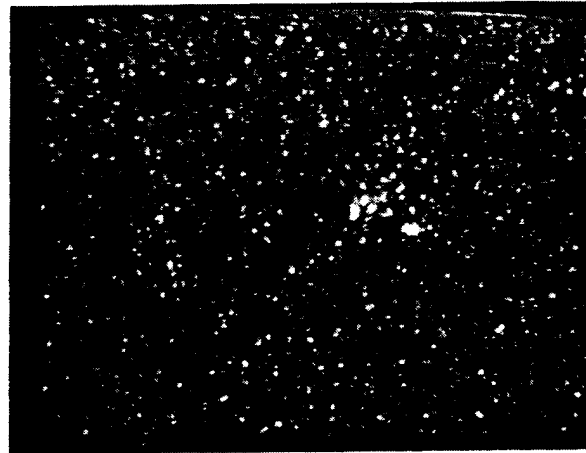
A 1/8 in. gas line from an N_2 cylinder regulated to a few psi provided pressure to drive vapor out of the cell. A solenoid valve in the line was attached to a 12 volt DC power



(a) before liquid deposited



(b) after liquid deposited



(c) after laser pulse

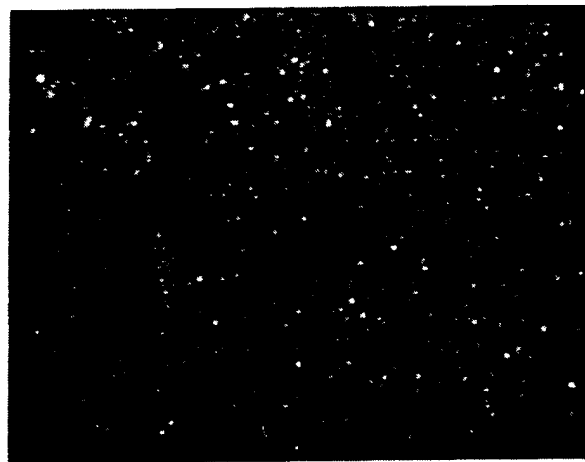


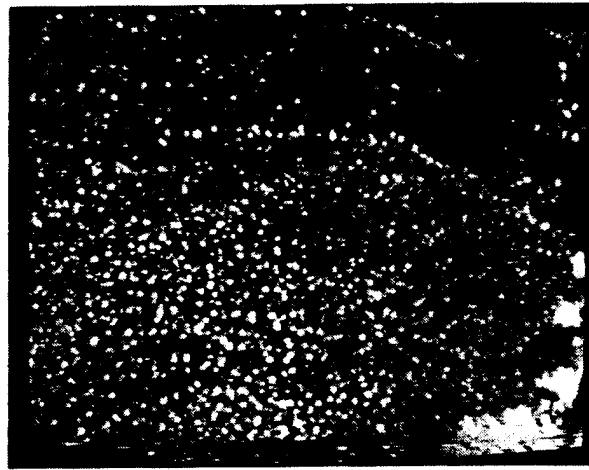
Figure 13. Video microscope records of particle removal from SS-304 (0.17 J/cm^2).

The beam fluence used was nominally 0.17 J/cm^2 , which left no surface marking.

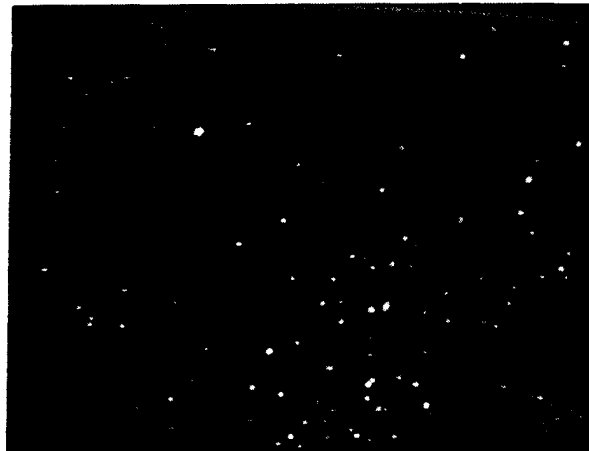
The series of photographs in Figure 14 shows the successful removal of hundreds of particles from a 52100 bearing steel substrate using a nominal fluence of 0.33 J/cm^2 . No surface marking of the substrate was detected.

The concept of removing micron size particles from metal substrates at $1.06 \mu\text{m}$ was successfully demonstrated. The fluence levels required for removal do not mark substrate

(a) before liquid deposited



(b) after one laser pulse



(c) after second laser pulse



Figure 14. Video microscope records of particle removal from smooth 52100 bearing steel (0.33 J/cm^2 , width of frame is 1.4 mm).

5.0 Conclusions and Recommendations

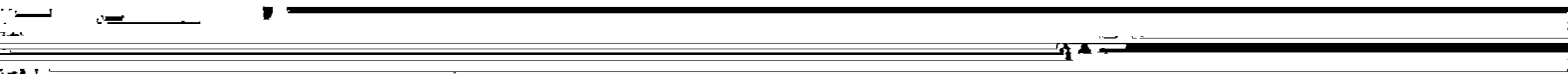

Based upon this initial research on advanced technology cleaning for guidance system components it was concluded that:

- (1) Plasma cleaning is well-developed and may be applicable to a few AGMC cleaning tasks where thin contaminant films must be removed from large areas and cleaning time is not a factor. An example might be final preparation of a glass filter plate for an adhesive bond to a CRT faceplate.
- (2) Plasma cleaning is not generally applicable to the removal of thick layers of residues and contaminants (such as epoxy bond residues and screw staking residues) because of the very slow (atom by atom) removal rates.
- (3) A new laser cleaning technique has been demonstrated that removes large epoxy layers (up to 0.013 in. thick) and patches cleanly from metal substrates with no liquids involved and no vapors generated. The removal occurs in a single laser pulse if the irradiance area covers the entire patch.
- (4) The threshold for debonding epoxy (LCA-9, LCA-4, FA-8) from SS-304 is about a factor four below the micromelt threshold for 10 ns pulses and about a factor of seven below for 1 ms pulses at 1.06 μm .
- (5) The debonding threshold did not depend significantly on laser wavelength and did not vary among the epoxies studied. The lower threshold for micromelt at the shorter wavelengths suggests that 1.06 μm (or longer) is the best choice of wavelength for epoxy debonding.

- (6) Laser exposures of P-37 potting compound suggest that it does not cleanly ablate at 1.06, 0.53, or 0.355 μm . The material chars and forms craters at very high fluences. These wavelengths cannot be used for etching out cracks, but they may remove thin layers from metal in a manner similar to the epoxy debonding process.
- (7) The particulate removal process discovered at IBM for silicon substrates using UV lasers has been demonstrated for two steel substrates using 1.06 μm laser pulses for the exposure. Micron and submicron silica particles were cleaned from the surface with only a transient film of water/ethanol mixture (80/20) and a single laser pulse with fluence below the substrate marking threshold fluence.

To benefit from this initial phase, it is recommended that additional research and development be undertaken to:

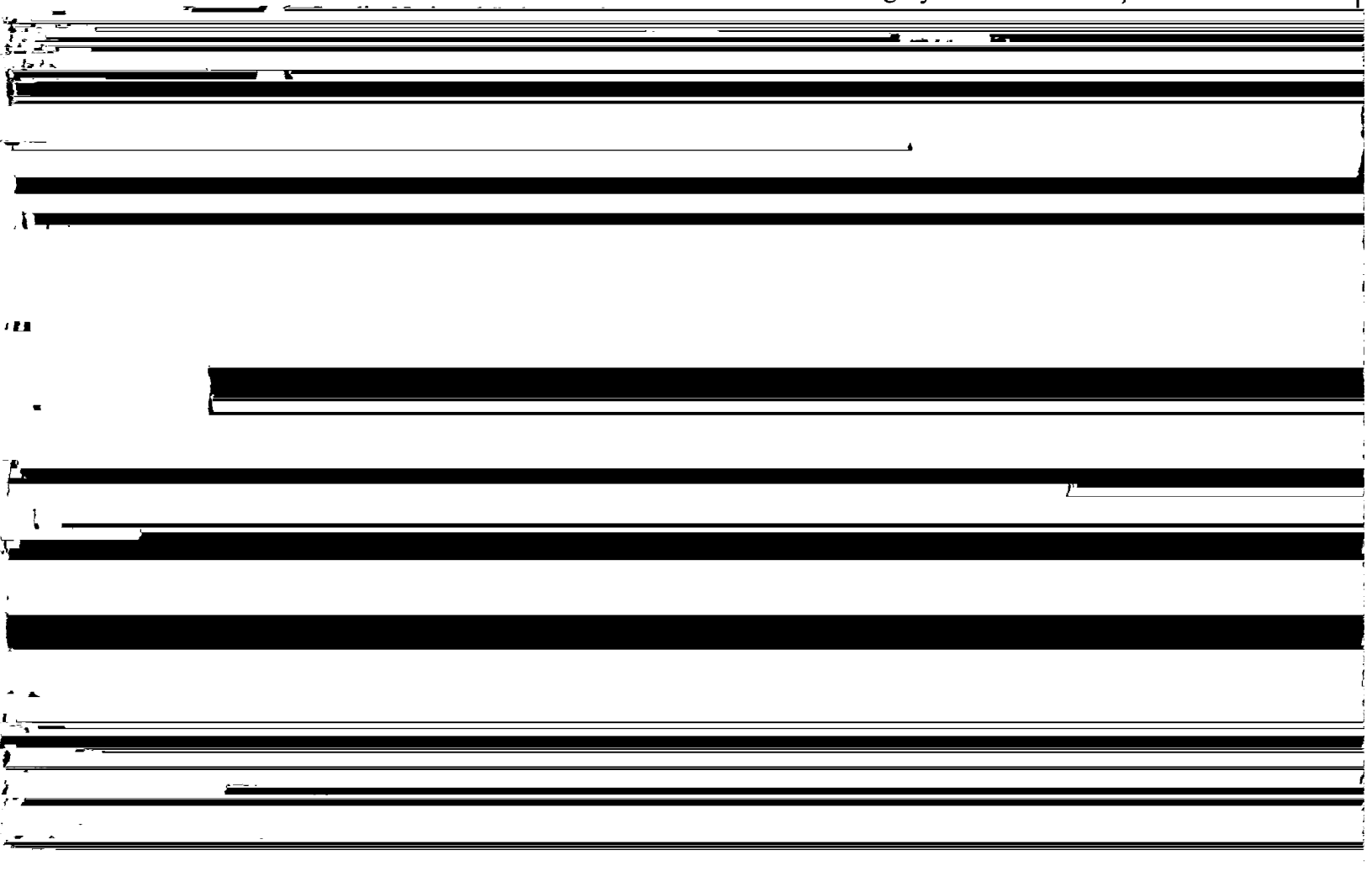
- (1) further characterize and validate epoxy removal tasks at AGMC that would be
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- (2) further characterize and validate particulate contaminant removal tasks at AGMC
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- (6) perform laser cleaning trials at AGMC and assess both cleanliness levels achieved and operational characteristics obtained in a production environment, and
- (7) implement any system modifications required and integrate laser cleaning into production operations.

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